

Performance Testing of Lithium-Ion Cells at JPL for Future NASA Aerospace Applications

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INTRODUCTION

NASA requires lightweight rechargeable batteries for future missions to Mars and the outer planets that are capable of operating at low temperatures. Due to the attractive performance characteristics, lithium-ion batteries have been identified as the battery chemistry of choice for a number of future applications, including Mars Rovers and Landers. Under an Interagency program, lithium-ion cells of varying capacity are being developed for NASA and DOD applications. JPL, in collaboration with Wright Patterson Laboratory (Air Force), is currently evaluating a number of lithium-ion cells varying in capacity from 3 Ah to 40 Ah for future aerospace applications. The Mars Lander and Rover applications require a rechargeable high energy density system capable of operation at temperatures as low as -20°C . Future Orbiter applications require high energy batteries which exhibit long cycle life ($> 20,000$ cycles at low depths of discharge) and long calendar life (10-20 years). To assess the viability of lithium-ion cells for these applications, a number of performance characterization tests have been performed, including: assessing the room temperature cycle life, low temperature cycle life (-20°C), rate capability as a function of temperature, pulse capability, self-discharge and storage characteristics, as well as, mission profile capability.

CELL TESTING PROCEDURES

In order to assess the viability of using lithium-ion technology for future NASA and DoD applications, a number of standard performance evaluation tests were implemented on cells received. This enables one to obtain comparative data which is helpful in comparing performance characteristics of cells of varying chemistry, cell size, and cell design. The cell testing procedures generally consist of performing: (a) 100% DOD cycling at different temperatures (-20 , 23 , and 40°C), (b) variable temperature cycling tests, (c) LEO cycling test under various conditions (d) discharge and charge rate

characterization at different temperatures (-40 , -30 , -20 , 0 , 23 , and 40°C), (e) storage characterization tests under various conditions, (f) and other mission specific testing. In addition to these standard tests, other characterization tests were performed on selected samples to determine: (i) the effect of charge methodology, (ii) the effect of temperature extremes upon performance, and (iii) the thermal behavior of lithium ion cells. Depending upon the number of samples received in a typical cell lot, the types of tests performed were prioritized and considered with relation to the relevance of up-coming applications.

100% DOD CYCLE LIFE PERFORMANCE AT DIFFERENT TEMPERATURES

In order to determine the life characteristics of the prototype cells received, 100% depth-of-discharge (DOD) cycle life tests were initiated at a number of different temperatures. These tests typically consist of cycling the cells between the voltage range of 3.0V and 4.1V using a C/5 charge current and a C/5 discharge current. The cell charging protocol consists of constant current charge to the desired potential follow by a constant potential step with a taper current cut-off of C/50. When the room temperature cycle life performance of various prototype cells are compared using this testing regime, very similar results were obtained regardless of cell size, type, or vendor. As shown in Fig. 1, when the discharge capacity is normalized comparable performance was obtained with a number of cells under 100% DOD cycling conditions at room temperature.

Unlike Ni-based battery systems, lithium-ion delivers excellent coulombic efficiency ($>99\%$) over a wide temperature range. As shown in Fig. 2, the charge/discharge ratio is relatively unchanged over the lifetime of 100% DOD cycling. In some cases, however, there is more scatter and fluctuation of values late in life suggesting some connection with cell degradation mechanisms.

However, the watt-hour efficiency, or round-trip efficiency, is not as high as the coulombic efficiency and is observed to noticeably decrease as a function of lifetime, as shown in Fig. 3. This trend can be understood in relation to the observed impedance increase of cells upon cycling, implying that increased resistivity due to continued passivation of the electrode materials resulting in increased polarization effects. In terms of operation, this also implies that heat generation rates will be greater at later stages in cell life, which can have implications for thermal designs in potential applications.

In addition to the room temperature cycling tests, 100% DOD cycling tests were performed at -20°C , where both charge and discharge were performed at low temperature in a convectively cooled environmental chamber. Low temperature cycle life evaluation is especially important with respect to upcoming NASA applications, such as Mars Landers and Rovers, which require operation to temperatures as low as -20°C . These tests generally consisted of charging the cells at a C/10 rate to 4.1 V (with a C/50 cut-off) and discharging the cells to 3.0V. Although it has been demonstrated that a substantial increase in capacity can be obtained upon discharging below 3.0 V (i.e., 2.5 V), most of the applications dictate a 3.0 V minimum for operation of individual cells (and the corresponding battery voltage). As shown in Fig. 4, when the cycle life performance of a number of prototype lithium-ion cells is compared at -20°C it is evident that good performance was obtained in most cases with 70-80% of the room temperature capacity being delivered under these cycling conditions. Given that many of the upcoming planned missions have limited cycle life requirements of 200-300 cycles, the data supports that the technology can meet the life requirements.

As shown in Fig. 4, when the watt-hour efficiency is compared at different temperatures the inefficiency becomes more dramatic due to the increasing resistivity upon going to low temperatures. Similar to the discussion above, this also correlates to an increase in the heat generation rates of the cells upon going to lower temperature. This thermal aspect of lithium-ion cells is of some benefit when considered in terms of the low temperature performance, since the cells have some self-heating properties upon operation which helps to enhance the low temperature capabilities. In contrast, however, the heat generation rates are relatively low at higher temperatures, which helps to simplify battery thermal designs.

LEO CYLING PERFORMANCE

Although many of the upcoming Mars missions only require operation for 200-300 cycles once upon the surface of Mars, other potential applications require much longer cycle life performance, i.e., 10,000 – 30,000 cycles and a 10-20 year calendar life. For most of these

applications, however, the cycling required typically corresponds to a shallow depth of discharge ($<50\%$ DOD). In order to assess the viability of using lithium-ion technology for such missions, such as Mars orbiters, low earth orbit (LEO) cycle life testing was performed under various conditions. As shown in Fig. 8, when a prototype 25 Ahr cell was cycled at room temperature using a 30% DOD cycling regime good performance was obtained with nearly 9,000 cycles being completed to date without falling below 3.0 V. This test was performed by charging the cell with 0.4 C constant current to 4.1 V for a total charge time of one hour and discharging the cell at a 0.6 C rate for 30 minutes. Since a fixed amount of capacity is discharged each cycle, corresponding to 30% of the nominal capacity, the cell capacity fade characteristics can be monitored by observing the end of discharge voltage.

It is generally accepted that the best cycle life performance under this type of testing regime can be obtained by cycling the cells at lower temperatures ($0-10^{\circ}\text{C}$), charging at lower voltages, and cycling at a low DOD. In an attempt to determine the impact of these variables, a number of cells are currently being cycled at different temperatures, different SOC, and using different charge voltages. As shown in Fig. 9, generally good performance has been obtained over a limited amount of cycles. Although the cells cycled at lower temperatures (i.e., 0°C) and using lower charge voltages (i.e., 3.85 V) deliver lower specific energy, they are anticipated to have longer life characteristics overall.

DISCHARGE AND CHARGE CHARACTERISTICS AT DIFFERENT TEMPERATURES

In addition to routinely evaluating the cycle life performance of prototype cells, discharge rate characterization was performed at a number of different temperatures ($-30, -20, 0, 23$, and 40°C). Due to the fact that most of the prototype cells received were fabricated with the intention of providing good low temperature performance, in an attempt to meet the requirements imposed by the upcoming Mars mission, a large amount of attention was placed upon fully characterizing the performance between -40 and 0°C . As shown in Fig. 10, excellent performance was obtained in some cases with approximately 80 Wh/Kg being delivered at -30°C using at C/5 discharge rate to 3.0V. These results are especially significant considering that the cells are also charged at the respective temperatures (C/10 charge current to 4.1 V).

In general, excellent low temperature performance was obtained with a number of different cell designs which were provided from a number of different vendors. The improvements in the low temperature capability of prototype lithium-ion cells in recent years has been primarily achieved by the use of electrolytes which were developed specifically to enable operation at low temperature. Although excellent performance was

obtained in many cases, it was observed that the low temperature capability of many cells declined with cell age, which was accelerated upon exposure and/or operation at high temperatures ($>23^{\circ}\text{C}$). As shown in Fig. 11, the discharge capacity/energy delivered by a prototype cell at -20°C dramatically declines after being cycled at 55°C (8 cycles). Our findings from tests focused upon trying to understand the effect of high temperature exposure upon performance suggest that keeping the cells in a low state-of-charge and non-operative during these excursions is preferable. In order to quantify the diminishment of low temperature capability as a result of high temperature cycling and/or exposure, we have cycled a number of cells between temperature extremes (-20 and 40°C) for fixed number of cycles at each respective temperature (10 or 20). Such standardized tests allow us to make comparative assessments of different cell chemistries and cell designs with respect to the sensitivity of the low temperature performance to high temperature exposure.

Charge rate capability as a function of temperature was also evaluated for a number of cells. Since the cells were typically charged using a modified constant potential charge, generally very comparable capacities were obtained at a specific a temperature regardless of the rate of constant current initially imposed. However, greater differences were noticed on the amount of capacity which was accepted in the constant potential mode in contrast to the constant current mode of the two step charge methodology. At lower temperatures and later in life, the cells generally display poorer charge acceptance characteristics, reach the constant potential charging regime much quicker, and take longer to charge. In addition, when the temperature is low enough (-20 to -40°C) many of the cells are unable to sustain high charge currents (over $C/5$) for any significant length in time and the bulk of the charging involves low current ($< C/10$). While charging at these very low temperatures, it is generally preferred to use moderate to low charge rates (and/or low charge voltages) to avoid the possibility of plating lithium upon the anode under forcing conditions.

In evaluating the 100% DOD cycle life performance at various temperature, the charge methodology typically employed consists of terminating the charge once the current has decayed to $>C/50$. Since a number of upcoming NASA and DOD missions will involve designing the battery such that it will be permanently attached to the bus, it was desired to obtain cycling data under conditions in which the charge periods were much longer. When cells were cycled using a long charge period (20-24 hours) where the cells were held at constant potential for the bulk of the charge, no effect upon the capacity fade characteristics were observed over hundreds of cycles. This is encouraging due to the fact that one would expect that the cell degradation would increase due to being held at high potential for long periods of time.

STORAGE CHARACTERISTICS

For many future applications of lithium-ion technology, good storage characteristics, or shelf life, is required. For example, the Mars Landers and Rover require the battery to be able to withstand a 10-11 months cruise period while the spacecraft is en route to Mars. In addition to this cruise period, there will be some time between cell fabrication and the actual launch date. Thus, the cells/batteries developed for these missions must be able to withstand a ~ 2 year storage period prior to meeting the requirements on the surface of Mars. Other future NASA missions, such as missions planned to the outer planets, have even more demanding requirements in terms of shelf life and require operation after 6-9 years after initial cell fabrication. Thus, in order to address the ability of lithium-ion technology to meet these requirements, a number of storage tests have been performed and are on-going. Effort is focused upon trying to determine the best conditions of storage. This involves determining the effect of storage temperature, state-of-charge, and method of storage (i.e., under OCV condition, connected to the buss, or subjected to low rate cycling) upon the performance characteristics. During the course of these investigations, it was observed that generally the best performance is obtained when the cells are stored at low temperatures, low SOC, and connected to the buss. For example, minimal capacity loss (2 to 4% reversible capacity loss) was observed with cells that were stored at 10°C on the buss at 70% SOC for one year.

MISSION SPECIFIC TESTING

In order to determine the ability of lithium-ion technology to meet specific mission requirements, a number of specialized tests which simulate actual mission conditions were performed in many cases. For example, development of the Mars Surveyor 2001 Lander battery involved testing cells according to a temperature profile and load profile which simulates the conditions expected to be encountered on the surface of Mars. According to the current estimates of the Martian surface temperature profile, and the corresponding temperature swings that will be experienced within proposed thermal enclosures, the battery is expected to operate over a large range of temperatures ($\Delta 60^{\circ}\text{C}$). To address this, continuous cycling of the cells between these temperature extremes (-20° to 40°C , corresponding to a typical Martian sol), was undertaken. This testing regime was only implemented after cells had been subjected to a storage period which simulates the cruise period anticipated. As shown in Fig. 12, large capacity prototype lithium-ion cells were successfully cycled according to a Lander mission simulation profile, which involves continuously cycling between -20° to 40°C .

CONCLUSIONS

Lithium-ion cells and batteries are being developed by a number of vendors in the U.S. for a number of future NASA and DOD applications. These efforts are, in part, being supported by a NASA and US Air Force Interagency program which has been instrumental in producing aerospace quality cells. These cells have been demonstrated at JPL to have excellent performance characteristics enabling the realization of a number of future missions. A number of cell designs and cell chemistries have been demonstrated to have: (1) good 100% DOD cycle life characteristics over a range of temperatures, (2) good LEO cycle life performance, (3) good charge and discharge rate capability, especially at low temperatures, and (4) good storage characteristics. In addition, lithium-ion technology has been demonstrated to be viable for a number of future NASA missions, including Mars Landers and Rovers.

ACKNOWLEDEMENT

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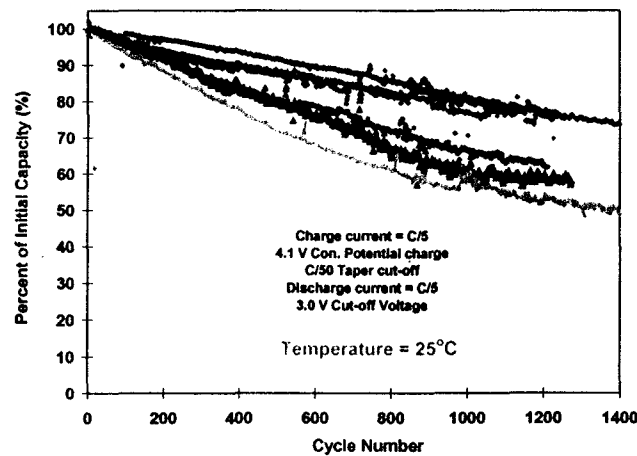


Fig. 1. Room temperature cycle life performance of various lithium-ion cells (different capacities, chemistries, and vendors) expressed in terms of the percent of initial capacity delivered.

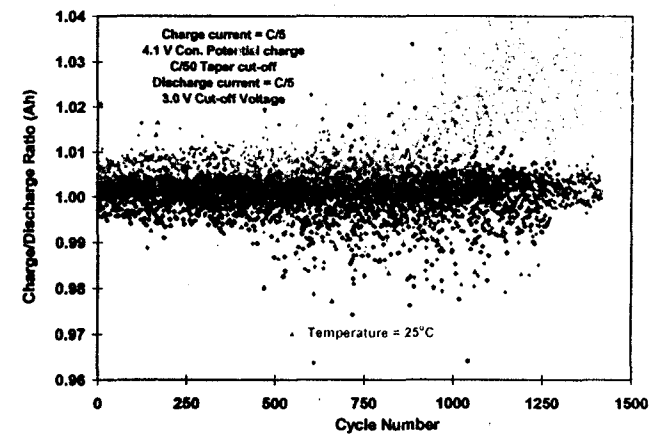


Fig. 2. Charge/discharge ratio of various types of lithium-ion cells subjected to 100% DOD room temperature cycling tests.

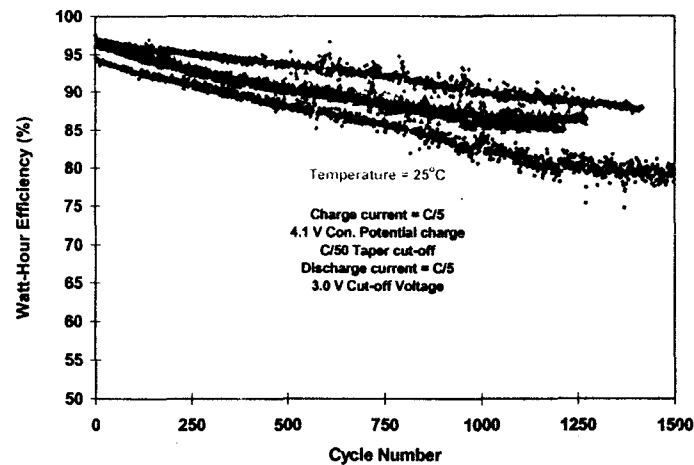


Fig. 3. Watt-Hour efficiency (or round-trip efficiency) of various types of lithium ion cells subjected to 100% DOD room temperature cycling tests.

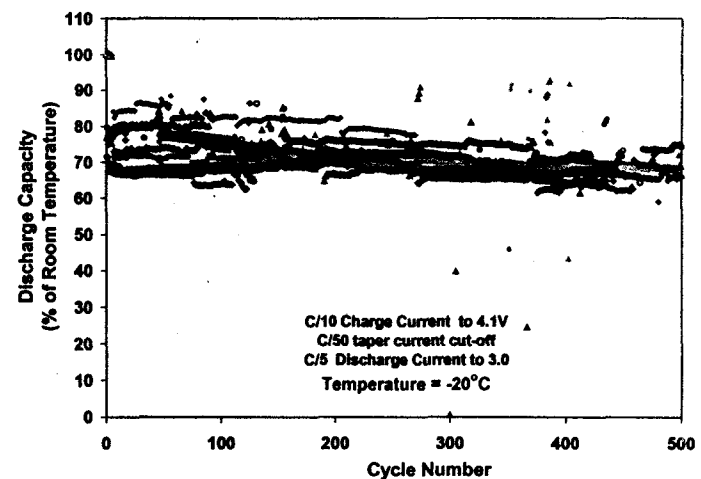


Fig. 4. Low temperature (-20°C) cycle life performance of various lithium-ion cells (different capacities, chemistries, and vendors).

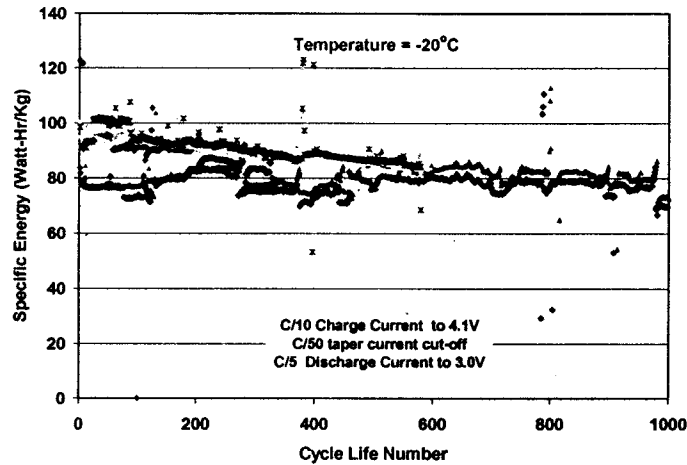


Fig. 5. Low temperature (-20°C) cycle life performance of various lithium-ion cells in terms of specific capacity delivered.

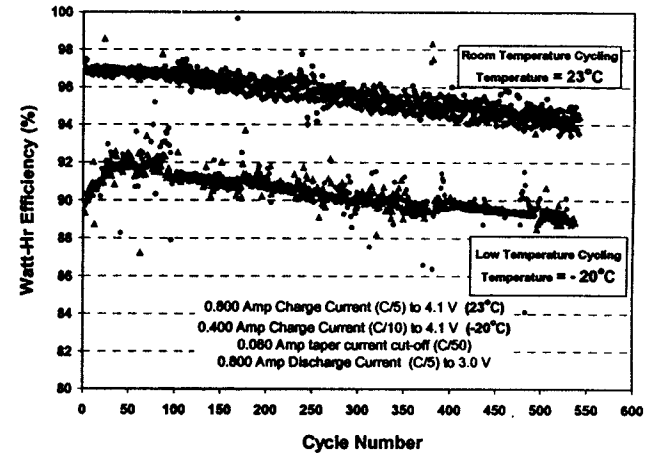


Fig. 6. Watt-hour efficiency of D-size cells at various temperatures subjected to 100% DOD cycling tests.

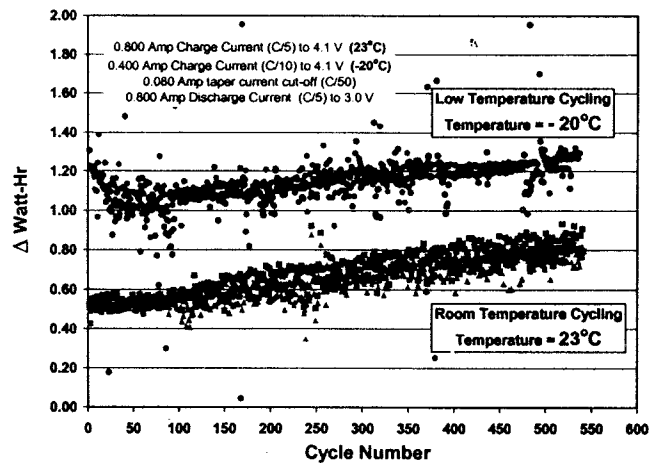


Fig. 7. Δ Watt-hours of D-size cells at various temperatures subjected to 100% DOD cycling tests.

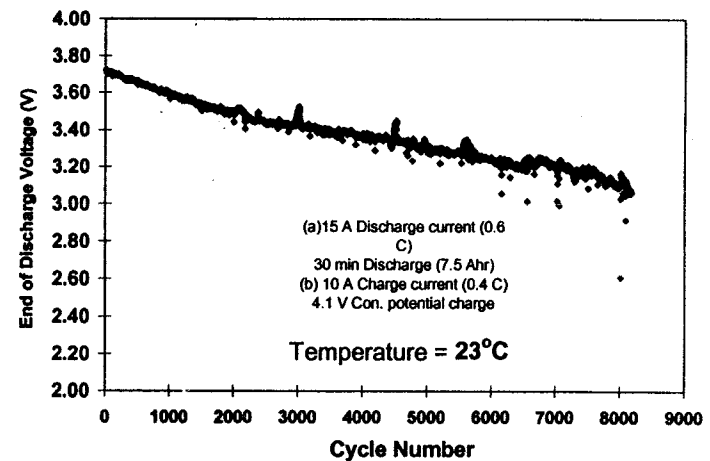


Fig. 8. LEO cycling (30% DOD) of a prototype 25 Ahr Lithium-ion cell at room temperature.

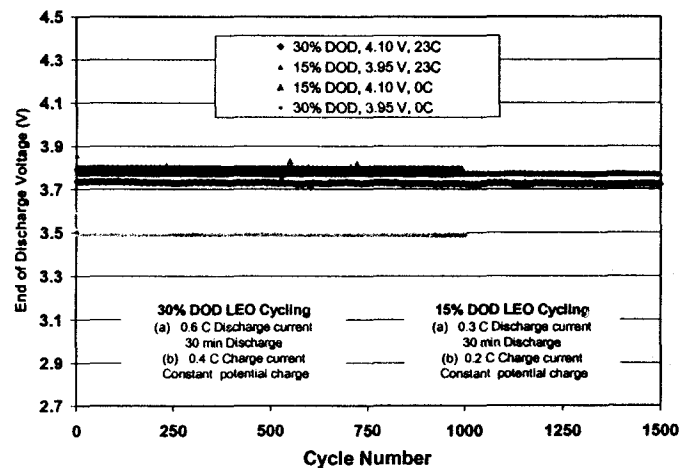


Fig. 9. Effect of temperature and DOD upon LEO cycling performance of prototype lithium ion cells.

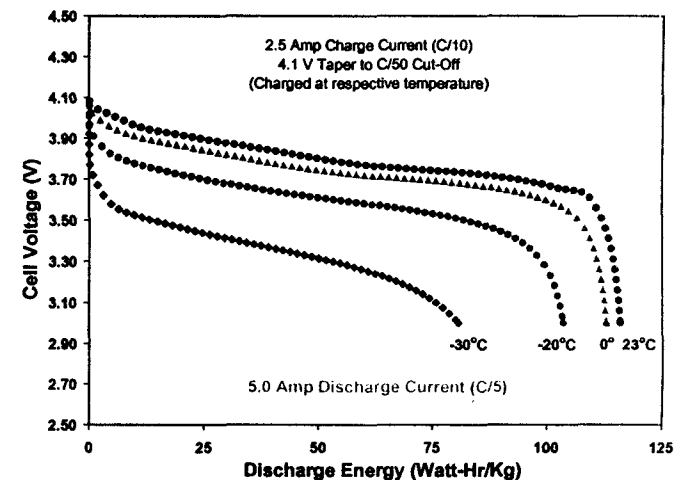


Fig. 10. Specific energy delivered by a prototype lithium ion cell at different temperatures (C/5 rate).

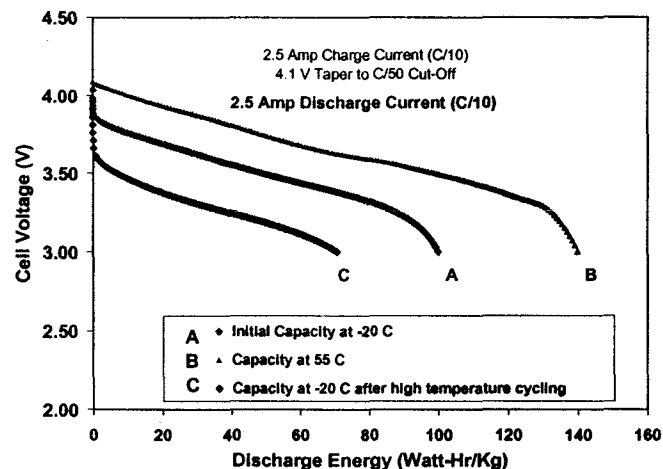


Fig. 11. Effect of high temperature cycling upon the low temperature performance of a prototype lithium-ion cell.

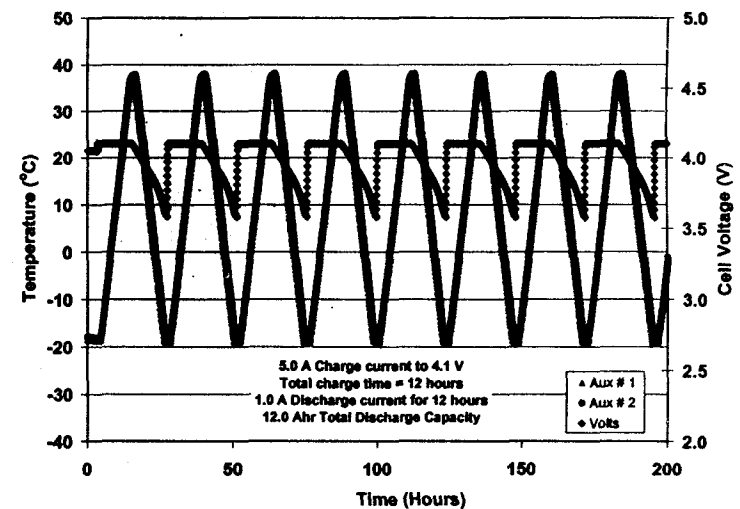


Fig. 12. Mission simulation cycling of large capacity lithium-ion cells after 1 year storage.